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PAPER

Correlation between specific ion adsorption at the air/water interface and long–range interactions in colloidal systems†

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Specific ion effects are of high impact in colloid science and dominate processes in aqueous systems from protein folding or precipitation to ordering of particles or macromolecules in bulk solutions. Due to the large internal interface of colloidal systems especially interfacial ion effects are of importance. This paper presents a new insight into the specific ion effects at the air/water interface of monovalent electrolyte solutions and their consequences for long-range interactions in colloidal systems. Solely, in an asymmetric film (*i.e.* wetting film) one can determine the sign and precise value of the surface potential of the free air/water surface. It is shown that the all over charges of the interfacial region, which are affected by the type of ion, dominate the interfacial forces even over several tens of nm. This is of interest for tailoring the stability of colloidal systems. It is clearly shown that the air/water interface is negatively charged and that both anions and cations affect the surface potential even at very low electrolyte concentrations (10^{-4} M).

1. Introduction

A lot of interfacial,[1,2] colloidal[3] and polymer[4] based phenomena are influenced by ion specific effects.

A synonym used for specific ion effects is the term "Hofmeister series". Franz Hofmeister investigated the ability of ions to precipitate egg-white proteins.[5] He classified anions in series like the following, ordered along their efficiency to salt-out proteins: SO_4^{2-} > F^- > Ac^- > Cl^- > Br^- > I^- > SCN^-. Typically, Hofmeister series are not unique. By referring to ion series instead of salt series, it is often neglected that ions cannot be considered as isolated species in water. Indeed, not only the type of ion considered is important for the ion specificity, but also the counteracting partner like a counterion or a surface being involved. Consequently, specific ion effects at the air/water and protein/water interface have to be different, even if the dielectric properties of both interfaces are similar. Ion-protein pairing is rather dominated by local interactions between functional groups at the protein surface and the respective ions than by the average dielectric properties of the protein and water.[6,7] Nevertheless, there is a strong similarity between the adsorption tendency of anions at protein surfaces and at the air/water interface. Therefore, the key to understand Hofmeister effects is thought to be found by investigating ion adsorption at hydrophobic interfaces, *e.g.* at aqueous interfaces. Since new surface selective spectroscopic techniques and computational methods enable the investigation of aqueous interfaces on a molecular level, good progress was made in studying the air/water interface. Those theoretical and experimental studies showed that cation effects are less pronounced than the one of anions since anions are larger and their radii vary stronger. Further, such studies indicated the adsorption of those large anions (with low charge density) to the outermost layer of the liquid/air interface.[1,8–15] Interestingly, recent studies of alkali and halide ions at the air/water interface using novel *non*-polarizable ionic force fields showed that cations can affect the properties of the air/water interface, as well.[16] Those studies have indicated that Li^+ is even less repelled than the larger Na^+ leading to a correctly inverse Hofmeister series. It is assumed that Li^+ appears larger due to its strongly bound first shell of water molecules.[16] This is contradictory to the common opinion that ion affinity for an interface derives from the interaction of the polarizability of the ion with the interfacial electric field due to the dipolar orientation of interfacial water molecules.[17,18] Obviously, it depends on the environment, since for polyelectrolyte multilayers no specific property of the Li could be figured out.[19]

All findings described so far mention an excess of ions at the air/water interface. This is in contradiction with the textbook description of ions being repelled from the interface and the outermost surface layer being depleted by ions.[20–22] This traditional interpretation is based on macroscopic measurements of increasing surface tension with the concentration (activity) of many inorganic salts, including the alkali halides. According to

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† Electronic supplementary information (ESI) available: The theoretical model used for the calculation of the surface potentials at the air/solution and solution/solid surface which was carried out on basis of the non-linear Poisson Boltzmann model for two charged surfaces in electrolyte solutions (section 1) and the results of zeta-potential measurements of silica particle in 10^{-4} M electrolyte solutions (section 2). See DOI: 10.1039/c0sm01162b

the Gibbs model,[23] such measurements dictate a negative surface excess of ions. The interpretation of the macroscopic results in terms of a non monotonic ion density profile with surface enhancement and subsurface depletion shows that the theoretical and experimental findings mentioned above do not contradict the surface tension measurements and thermodynamic arguments.[24] Furthermore, Pegram and Record developed a thermodynamic partitioning model (SPM) using electrolyte surface tension gradients to derive surface partitioning of individual ions at the air/water interface.[14,25,26] The contributions to the electrolyte surface tension gradients of each ion present can be treated as independent and additive up to concentrations below 1 mol kg^{-1}. This surface partitioning model results in a relative order of ion affinities for the surface, for cations and anions.

For the stability of colloidal systems interfacial forces of a length scale of several tens of nanometres are important. Therefore, the charge average across the whole interfacial region is of interest. Wetting films comprises the striking advantage that the sign of the potentials of opposing surfaces can reliably be determined. Moreover, single wetting films are unique for studying aqueous films without any stabilizers (*i.e.* surfactants). With respect to technical applications a proper understanding of specific ion effects on wetting phenomena is vital for the control of *e.g.* atmospheric aerosols,[1] heterogeneous catalysis,[27–29] froth flotation[30–32] and interactions between macromolecules and ions.[4]

In the present paper the influence of anions and cations on the air/water interfacial region is investigated by using a modified TFPB technique for wetting films (air/liquid/solid). Thin wetting films formed from aqueous electrolyte solutions without any surfactant have been studied in a number of papers.[33–41] Until now, the measurements of aqueous wetting films were predominately used to clarify wettability on modified solid substrates[34,35,40–42] in order to detect the surface forces acting in wetting films[36,37] and to validate theoretical models for example of rupture mechanism.[38] Few authors were interested in specific effects of ions on the stability and thickness of aqueous wetting films.[31,35,41] Read and Kitchener investigated wetting films of KCl, $BaCl_2$ and $LaCl_3$ solutions on glass.[31] They found that the equilibrium wetting films of KCl solutions are more than 10 nm thicker than of $BaCl_2$ at the same ionic strength. An interpretation of their findings according to specific ion effects failed, because of a lack of supporting data like reliable potentials for the considered interfaces.

This work addresses the question: "How do ions influence the properties of the air/water interface and thus the stability and thickness of wetting films?" Since the air/water interface is negatively charged the question arises if the impact of cations and anions on the properties of this interface is dominated by electrostatic interactions or due to the ion specificity and what are the consequences regarding film stability and thickness of thin aqueous wetting films. Therefore, salt effects on the film thickness and stability of wetting films formed between aqueous electrolyte solutions and a silicon wafer with native oxide layer are examined within this paper. For this purpose, disjoining pressure isotherms (Π *vs.* film thickness h) of various monovalent salts at a fixed concentration of 10^{-4} M are recorded by using a modified TFPB. This technique has successfully been used by the authors to probe the existence of negative surface charges at the air/water interface.[40,41]

2. Materials and methods

2.1. Materials and cleaning procedure

Electrolytes with purity >99.9% were obtained from Merck (Germany). Wherever possible, the salts were roasted to remove organic contaminants. Roasting was carried out for 24 h at 500 °C. All solutions were prepared with Milli-Q® water at a fixed concentration of 10^{-4} M. The electrolyte solutions have a pH of about 5.5. Silicon wafers used as solid substrate were cleaned with a 1 : 1 mixture of H_2O_2/H_2SO_4 (30 min) followed by extensive rinsing with Milli-Q water. In the pH range used the silicon substrate is negatively charged since the zero point of charge (z.p.c.) is thought to be at pH 2–3.[30] All glassware (except the film holder) was cleaned with piranha solution (1 H_2O_2:1 H_2SO_4) for 20 min and rinsed thoroughly with water before use.

2.2. Disjoining pressure and film thickness

All wetting films of electrolyte solutions were measured in a modified thin film pressure balance (TFPB)[39] using the porous-plate technique to determine the disjoining pressure, Π, as a function of the film thickness, h.[43–45] The film is formed in a hole of 1 mm in diameter drilled into the porous glass disk. The film holder is placed in a hermetically sealed and temperature controlled stainless steel cell in such way that the film is exposed to the gas pressure and the free end of the film holder's glass tube is exposed to the atmospheric pressure. The pressure can be adjusted *via* valves by a high sensitive pressure transducer. In order to adapt the TFPB apparatus for studies of wetting films, a solid substrate (silicon wafer) is attached beneath the modified film holder by adhesion forces.[40,41] $\Pi(h)$ curves are generated by interferometrically measuring the film thickness after applying a fixed pressure in the cell. The equilibrium film thickness is thought to be reached when the intensity of the reflected light is constant over a time period of 20 min. Before the film is formed, the film holder is immersed into the solution for at least 2 h. All measurements were performed at 23 °C. All curves are fitted by solving the non-linear Poisson Boltzmann equation for two dissimilarly charged surfaces in electrolyte solutions (supplementary information).[46–49] The surface charge densities are calculated by the well-known Grahame equation[50] from the potentials and the ionic strength resulting from the simulations.

3. Results

The present paper deals with specific ion effects on the stability and thickness of aqueous wetting films on silicon with a native oxide layer at a fixed electrolyte concentration of 10^{-4} M. All isotherms depicted in the following are averages of at least three separate experiments. In contrast to symmetric films,[51] asymmetric films of aqueous electrolyte solutions at low concentrations can be stable without any surface active additive. Within one group of experiments either the cation or the anion was varied in order to distinguish their ion specific effects.

3.1. Anion effects

The influence of different negative ions on the stability and thickness of thin aqueous wetting films is illustrated in Fig. 1. It

shows disjoining pressure isotherms of potassium salts (filled symbols) at a fixed ionic strength of 10^{-4} M and of a pure water film (open diamonds) as reference system. The film thickness and stability decreases in the order iodide, chloride and fluoride. The changes in thickness are far beyond the range of measuring inaccuracy. The maximum pressure which can be applied to potassium films before they rupture decreases from $\Pi_{max} = 1385$ Pa for iodide to $\Pi_{max} = 630$ Pa for fluoride. The water film persists stable up to a maximum disjoining pressure of $\Pi_{max} = 2760$ Pa with a thickness which is intermediate between the film thickness of KI and KCl. Simulations of the disjoining pressure isotherms lead to the result that the potential (Φ_{01}) at the air/solution interface increases from 105 mV for wetting films containing KF, over 125 mV for KCl to 135 mV for KI, while the potential of the solution/solid interface (Φ_{02}) remains constant at 85 mV. The results of the simulations are presented in Table 1. The theoretically calculated Debye length of the corresponding bulk solutions with an ionic strength of 10^{-4} M is 30 nm. The Debye length obtained from the simulations of the isotherms varies between 23 and 30 nm for the films containing potassium salts. The Debye length for potassium iodide and chloride films with 29 nm are similar to the theoretical value. Only the one of the potassium fluoride films is shorter (25nm). The disjoining pressure isotherm for a pure water film is flatter, which indicates a longer Debye length (about 40 nm) due to a lower ionic strength.

To summarize: with increasing size of the anion the wetting films become thicker, more stable and the potential at the air/solution interface increases.

3.2. Cation effects

Two different series of disjoining pressure isotherms were measured where the cations are varied and the anions are fixed. The results for iodide salts are depicted in Fig. 2. The maximum pressure before the rupture of aqueous wetting films of iodide salts occurs decreases from $\Pi_{max} = 2323$ Pa for sodium iodide to $\Pi_{max} = 1093$ Pa for caesium iodide. Generally, the thickness of iodide films decreases with increasing size of the cation in the order sodium, potassium and caesium. The thickness of iodide films before film rupture occurs is about 60 ± 5 nm and similarly decreases with increasing ion size. The potentials obtained by simulations follow the trend observed for the stability and thickness of aqueous iodide salt films: The potential also decreases with increasing size of the cation, 140 mV (Na^+) > 135 mV (K^+) > 115 mV (Cs^+) (see Table 1). The Debye length of disjoining pressure isotherms of all iodide solutions is 29 nm, which agrees with the theoretically calculated value for the corresponding bulk solutions at an ionic strength of 10^{-4} M.

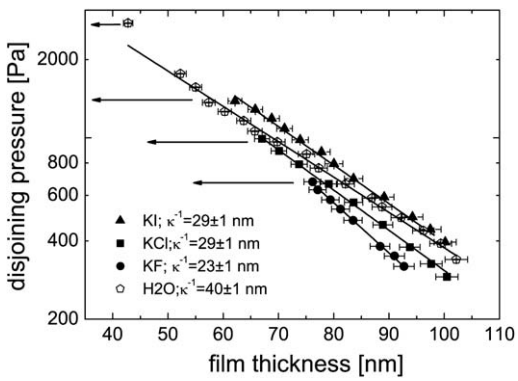

Fig. 1 Disjoining pressure isotherms of aqueous films on silicon with a native oxide layer: pure water (open pentagons) and aqueous solutions of potassium fluoride (filled circles), chloride (squares) and iodide (triangles) at a fixed concentration of 10^{-4}M. The respective pressure values before the film ruptures are indicated by the arrows. The solid lines corresponds to the simulations according to the solution of the non-linear Poisson Boltzmann equation for dissimilar surfaces.

The data obtained with fluoride salts are shown in Fig. 3. The film thickness and stability decreases with changing the cation from sodium *via* potassium to caesium. Wetting films of fluoride salt solutions are less stable (Π_{max} < 725 Pa) and rupture at thicknesses about 74 ± 5 nm. Simulations of the disjoining pressure isotherms show that the potential (Φ_{01}) at the air/solution interface decreases from 115 mV for wetting films containing NaF, over 105 mV for KF to 90 mV for CsF (see Table 1). In presence of fluoride the Debye length resulting from the simulation of the isotherms, is 23 nm. This is slightly different from the theoretical screening length that is 30 nm as mentioned above.

In summary, with increasing cation size, films become thinner and less stable. Hence the cation size has an opposite effect on film properties as the anion size.‡ The simulation results into the same sign for both interfaces. Since it is well known from streaming potential measurements that the potential of bare silicon (Φ_{02}) is negatively charged at pH 5.5 used in the present experiments, the air/water interface (Φ_{01}) has to be negatively charged as well.

The respective ionic strength from the fitting procedure for solutions containing fluorides is larger than expected from the fixed concentration (*i.e.* the Debye length obtained by simulation for fluorides are shorter than the theoretical value). A reason for this could be the neglect of ion–ion correlations and ion size effects in the model used. Therefore interfacial charges deduced from theses calculations should not be regarded as absolute values.

4. Discussion

The aim of this work was to clarify the influence of specific ions on the stability and film thickness of thin aqueous wetting films on silicon as solid substrate. Adding different monovalent ions has a pronounced effect on the stability and film thickness. The comparison of these results points out that the interaction of cations and anions appropriates the stability and thickness of the films as far as with increasing cation size and decreasing anion size the film thickness and the stability decreases due to the reduction of the surface potential and surface charge.

4.1. Anion effect

By keeping the positively charged ion constant, an increase in film thickness with increasing size of the negatively charged ion has been found. As previously reported by the authors, an

‡ The term "ion size" refers to the ion diameter without hydration shell.

Table 1 Experimental maximum pressure before film rupture Π_{max}, surface potentials Φ_{01} and Φ_{02}, surface charge densities σ_{01} and σ_{02}, and the corresponding Debye length κ^{-1} obtained by fitting the pressure isotherm of aqueous wetting films at a fixed concentration of 10^{-4} M using solution of the PB equation. Φ_{01} refers to the air/solution interface and Φ_{02} to the solution/solid interface

	Π_{max} [Pa]	Φ_{01} [mV]	Φ_{02} [mV]	σ_{01} [mC/m^2]	σ_{02} [mC/m^2]	κ^{-1} [nm]
H_2O	2760	130 ± 5	90 ± 5	5.54 ± 0.5	2.49 ± 0.5	40
KI	1385	135 ± 5	85 ± 5	8.43 ± 0.5	3.09 ± 0.5	29
KCl	790	125 ± 5	85 ± 5	6.92 ± 0.5	3.09 ± 0.5	29
KF	676	105 ± 5	85 ± 5	5.87 ± 0.5	3.90 ± 0.5	23
NaI	2323	140 ± 5	90 ± 5	9.30 ± 0.5	3.43 ± 0.5	29
NaF	725	115 ± 5	90 ± 5	6.59 ± 0.5	3.98 ± 0.5	25
CsI	1093	115 ± 5	80 ± 5	5.68 ± 0.5	2.78 ± 0.5	29
CsF	497	90 ± 5	80 ± 5	3.83 ± 0.5	3.10 ± 0.5	26

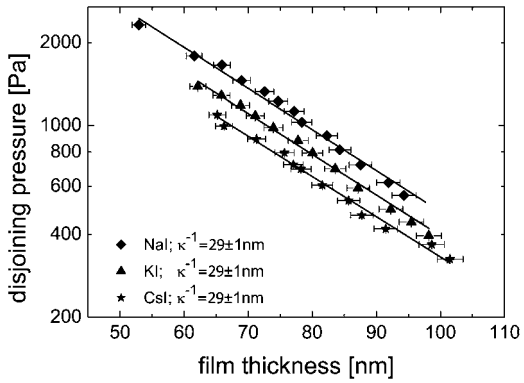

Fig. 2 Disjoining pressure isotherms of wetting films of sodium iodide (diamonds), potassium iodide (triangles) and caesium iodide (stars) solutions on silicon at fixed concentration of 10^{-4}M. The respective pressure values before the film ruptures are indicated by the arrows. The solid lines corresponds to the simulations according to the solution of the non-linear Poisson Boltzmann equation for dissimilar surfaces.

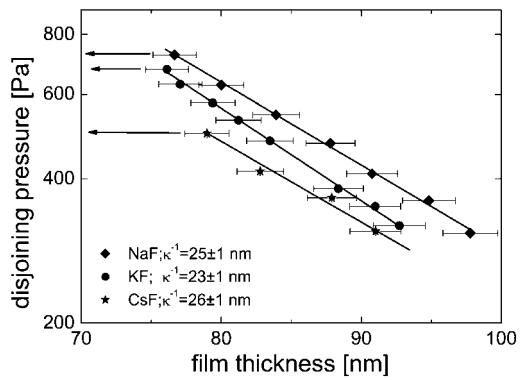

Fig. 3 Disjoining pressure isotherms of wetting films of aqueous fluoride solutions at fixed concentration of 10^{-4}M. The cations are varied from sodium (diamonds) *via* potassium (circles) to caesium (stars). The respective pressure values before the film ruptures are indicated by the arrows. The solid lines corresponds to the simulations according to the solution of the non-linear Poisson Boltzmann equation for dissimilar surfaces.

aqueous wetting film is stable on a negatively charged solid substrate due to electrostatic stabilization because of negative charges at the air/water interface.[40,41] The increase in thickness of KI-containing films in comparison to the pure water films' thickness results from the increase in surface potential due to an excess of iodide anions at the air/water interface.

Although, the air/water interface is negatively charged, additional negative charges can obviously adsorb to the interface. Consequently, the properties of the hydration shell of the ions dominate the electrostatics, *i.e.* ion specificity dominates electrostatic repulsion from the interface.

The accumulation of larger ions, such as Cl^-, I^-, at the air/water interface has also been probed by surface sensitive techniques like second harmonic generation (SHG) and sum frequency generation (SFG).[11,12,52–57] The air/solution interface was modeled *via* molecular dynamics simulation in slab geometry with polarizable potentials for water and ions. They conclude a positive adsorption of species of high polarizability due to the asymmetric and dipolar character of the surface while those ions interact only weakly with water.[2,6,8–10,24,58] Other simulations indicate that even non-polarizable anions are attracted by hydrophobic interfaces if their effective radius is chosen to be large enough.[59–61] Another popular explanation for enhancement of anions at the hydrophobic gas/liquid interface is, that small ions with a larger hydration shell and/or high surface charge density (cosmotropic ions/water structure maker) prefer to stay in water, while ions with a smaller hydration shell and low surface charge density (chaotropic ions/water structure breaker) will favor the hydrophobic air/water interface.[62–64] In other words, the interfacial layer repels hydrophilic ions while it attracts and partly dehydrates hydrophobic anions. Free energy is gained by releasing water molecules which return to bulk water.[65–67] Another theoretical examination show that dispersion forces play a dominant role in ion adsorption at hydrophobic interfaces.[68] According to Jungwirth *et al.* sodium chloride is considered as a neutral salt since both ions tend to adsorb in a so-called subsurface,[10,69] which is in contrast to I^- showing an excess at the air/water surface and F^- which is depleted.[10] Indeed, in the present study the disjoining pressure isotherm of water is closest to the one of NaCl, just that the sodium chloride film rupture at lower disjoining pressure and that the slope of its $\Pi(h)$ curve is steeper.[41] Generally, all slopes of the disjoining pressure isotherms of aqueous salt solutions are steeper than the slope of a disjoining pressure isotherm of pure water because of the screening of the electrostatic repulsion within the water film due to the addition of 10^{-4} M salt.

4.2. Cation effect

Cation effects are expected to be much smaller than anion effects due to their smaller size resulting in smaller differences in size. The larger the cations are, the more they prefer to be at or close

to the air/water interface which is in analogy as for anions. While accumulation of anions leads to an enhancement of the negative surface potential of the air/water interface, resulting in thicker and more stable films, the accumulation of cations at the surface decreases the surface potential leading to thinner and less stable films (see Table 1). The most different halide anions are I^- and F^-, because fluoride is depleted and iodide accumulated at the air/solution interface. Therefore iodide and fluoride were chosen to investigate cation effects. From molecular dynamics simulation by Jungwirth *et al.*, it has been concluded that the halide anion distribution in the interfacial region is strongly affected by the identity of the associated cation.[70] Of course, with increasing surface charge the counterion concentration increases in the interfacial region, as well. SFG measurements showed that larger cations have the propensity to be closer to the surface in contrast to small cations.[70]

To conclude, the film thickness and stability decreases due to the reduction of the surface potential at the air/solution interface with increasing ion size from sodium *via* potassium to caesium.

4.3. Aqueous wetting film stabilities

The thickness region at which rupture of wetting films occurs is often referred to a so-called critical thickness h_{cr}. First critical thicknesses were obtained for low disjoining pressures measured using captured and/or rising gas bubbles. The critical thickness for rupturing of water films on quartz is found to be about 40 ± 10 nm.[71] Critical thicknesses found in literature for similar salt solutions like in the present study are about 75 nm for 5×10^{-4} M NaCl on quartz[37] and for KCl films on polished vitreous silica.[31,72,73] These findings agree with the critical thicknesses observed in the present work. Usually, the rupture mechanism depend on nature of solid and of the liquid, the degree of surface hydrophobicity and on the type of adsorption layer with its morphology and chemical heterogeneity. Generally, two mechanisms are nowadays accepted: the nucleation mechanism and the capillary wave mechanism.[74] For the latter, the existence of attractive interaction forces between solid and gas is necessary like in the case of recharging quartz by adsorption of multivalent cations resulting in an attractive electrostatic interaction.[75,76] According to Schulz the nucleation mechanism postulates the rupture of wetting films on hydrophobic substrates due to large nanobubbles coming from the wetting film surface to a distance where a local metastable foam film is formed. After rupture of this foam film a hole with three phase contact replaces the nanobubble. If the hole is large enough, the three phase contact expands leading to dewetting of the solid substrate.[38,77,78] Rupture of the investigated films due to nucleation mechanism can be discarded since silicon is hydrophilic. All electrolyte solutions completely wet the solid substrate with contact angles close to zero. As mentioned earlier, in the present study, the film thickness and stability of the electrolyte wetting films is controlled by repulsive electrostatic double layer force and attractive van der Waals force,[79] but anyhow, the latter does not play a role in our cases because of its short range (<20 nm). The destabilization of aqueous wetting films must be induced by reduction of the net surfaces charges at the air/water interface. Since the ζ-potentials of silica particles in 10^{-4} M electrolyte solutions are only slightly lower than in pure water and show no dependence on the type of salt, a constant screening of the negative charges at the solid substrate can be assumed (supplementary information). This assumption is strengthened by the results obtained by the fitting procedure since the values for silicon (Φ_{02}) differ only in a narrow range. The effect of the different salts on the film thickness and the stability is thus ascribed to the properties of the air/water interface. This assumption is strengthened by the results of Henry and Craig who investigated bubble coalescence in various electrolytes, although their concentration (>0.1 M) were much higher than in the present case (10^{-4}M).[80,81] Recently, the observed ion specificity in bubble coalescence inhibition could be linked with the SPM developed by Pegram and Record.[14,25,26,81] It seems that bubble coalescence is inhibited when both ions are accumulated at or repelled from the air/water interface, while an asymmetrical ion distribution results in immediate bubble coalescence. In case of aqueous wetting films, the film stability decreases with increasing asymmetry of the ion distribution. The varying surface affinity of ions results in an asymmetrical distribution of anions and cations in the surface and subsurface layer and creates an additional electrical double layer in the interfacial region,[8] which could cause the observed destabilization of the wetting films. For iodide and chloride the Debye length is similar to the one predicted for the respective bulk solutions (30 nm). For fluoride it is shorter with 25 nm. These findings suggest that the approximations used in the Poisson–Boltzmann model like treating ions as point charges, neglecting ion-ion correlations results in a distinct deviation of the theoretical value and the measured value. Therefore it could be worth revisiting the thickness of electrical double layer including ion–ion correlations, volume effects and charge distribution.

5. Conclusion

Many experimental and theoretical results contradict each other concerning the ion adsorption at the air/water interface, since they are sensitive for different length scales. Some methods are only sensitive for the surface layer and not for subsurface layers, others are sensitive for both. For the stability of colloidal systems interfacial forces over a range of several tens of nanometres are important, and related to that an average surface charge across the complete interfacial region. In the presented work we are able to determine the overall charge of the air/water interface without and in presence of ions. Solely, in an asymmetric film (*e.g.* wetting film) one can determine the sign and precise value of the overall charge of the free air/water surface.

With increasing ion size, *i.e.* decreasing charge density, ions show a stronger tendency to adsorb at the surface. Enhancement of anions at the air/water interface leads to an increase in stability and film thickness due to an increase in surface potential. The same adsorption effect is found for cations, but with the reversed effect on the surface potential and thus on the film thickness and stability. This result is another proof for the existence of negative charges at the air/water interface. It is worth to note that anions have such a drastic effect at the air/water interface although it is negatively charged. This demonstrates the dominating effect of the hydration shell of ions over electrostatics on their adsorption at the air/water interface. The adsorption of monovalent cations in the interfacial region at least in the concentration regime used,

does not cause a charge reversal at the air/water interface as expected for multivalent ions. Nevertheless, the interplay of anions and also cations defines the stability and thickness of the films. The destabilization of those films is caused by the reduction of the effective charge, because previous results have indicated that the force between the two opposing surfaces in an aqueous wetting films is controlled by electrostatic repulsion.[40,41]

The paper shows clearly that the type of ion presents a tool for tailoring the thickness and stability of wetting films even at very low electrolyte concentrations of 10^{-4} mol l^{-1}. The air/water interface shows a strong selectivity for different ions which might be used for ion separation (*e.g.* removal of heavy metal ions from nuclear waste by ion flotation). The owing question is, if these findings can be transferred to other hydrophobic interfaces like solid surfaces (teflon, diamond) or the hydrophobic parts of proteins.

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